

**PREPARATION, CHARACTERIZATION AND PERFORMANCE OF
La DOPED SnO₂ CATALYTIC PELLET FOR DETECTION OF VOLATILE
ORGANIC COMPOUNDS**

ANG GAIK TIN

UNIVERSITI SAINS MALAYSIA

2010

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**Thesis submitted in fulfillment of the requirements for the degree of
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LIST OF ABBREVIATIONS

a.u.	Arbitrary unit
BJH	Barret-Joyner-Halenda
BET	Brunauer-Emmett-Teller
CA	Catalytic activity
CO ₂	Carbon dioxide
CH ₄	Methane
DC	Direct current
E _g	Band gap
EPA	Environmental Protection Agency's
FID	Flame ignition detector
FSP	Flame spray pyrolysis
FTIR	Fourier Transform Infrared
FWHM	Full width half maximum
GC	Gas chromatograph
GHG	Green house gases
GPIB	General Purpose Interface Bus
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
La	Lanthanum
lvm	Labview measurement format (Text format)
MS	Mass spectroscopy
MOS	Metal oxide sensor

N ₂	Nitrogen
NO ₂	Nitrogen dioxide
OH	Hydroxyl radical
O ₂	Oxygen
PBC	Periodic bond chains
PID	Photoionization detector
ppm	Parts per million
REO	Rare earth oxides
SGS	Semiconductor Gas Sensor
Sn	Stannum / Tin
SEM	Scanning electron microscope
SO ₂	Sulfur dioxide
TiO ₂	Titanium dioxide
TEM	Transmission electron microscopy
TPR	Thermal program reduction
VOC	Volatile organic compound
VOCs	Volatile organic compounds
WO ₃	Tungsten trioxide
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	Description	Unit
<i>at.</i>	Atomic	Dimensionless
[<i>C</i>]	Concentration of target gas	ppm
<i>e</i>	Electron	Dimensionless
<i>eV</i>	Energy barrier	kJ/mol
eV	UV radiation energy	Electron volts
<i>I</i>	Current	Ampere
<i>k</i>	Boltzmann constant	Dimensionless
<i>L</i>	Crystallite size	Å/ nm
<i>M</i>	Concentration of solution	Molar
<i>P</i>	Pressure	Torr
<i>P/P₀</i>	Relative Pressure	Dimensionless
<i>R</i>	Resistance	Ohm (Ω)
<i>R_A</i>	Resistance in air	Ohm (Ω)
<i>R_V</i>	Resistance in VOC	Ohm (Ω)
<i>RR_{VOC}</i>	Response ratio	Dimensionless
<i>R²</i>	R-square	Dimensionless
<i>S</i>	Sensitivity	Dimensionless
<i>S_{BET}</i>	BET surface area	m ² /g
<i>T</i>	Temperature	K
<i>V</i>	Voltage	Volt
<i>V_o⁻</i>	Oxygen vacancies	Dimensionless
<i>V_{tot}</i>	Total pore volume	cm ³ /g

$^{\circ}\text{C}$	Degree celsius	Dimensionless
ΔH_f	Energy formation per oxygen atom	kJ mol^{-1}
λ	Wavelength of $\text{CuK}\alpha$	\AA
β	Full width half maximum (FWHM)	Dimensionless
θ	Bragg angle	Dimensionless

PENYEDIAAN, PENCIRIAN DAN PRESTASI PELET BERMANGKIN SnO₂ DOP La BAGI PENGESANAN SEBATIAN ORGANIK MERUAP

ABSTRAK

Pelet bermangkin berasaskan SnO₂ dengan tambahan 0-10 atomik % lanthanum disediakan dengan kaedah sol gel dan dicirikan dengan pembelauan sinar-X (XRD), mikroskop elektron transmisi (TEM), analisis permukaan (Nitrogen jerapan-desorpsi) dan pengimbasan mikroskop elektron (SEM). Sebelum pengukuran sensor gas, perisian LabVIEW telah digunakan untuk mendapat semua nilai rintangan yang telah diukurkan atas pellet bermangkin. Perubahan rintangan elektrik oleh pelet bermangkin dikajikan dengan menggunakan wap sebatian organic meruap (VOC) iaitu etanol, aseton dan metanol dalam udara pada suhu antara 150-350°C.

Kepekaan dari pelet bermangkin SnO₂ telah ditingkatkan dengan penambahan lanthanum. Kepekaan sebanyak 50.52 telah dicapai oleh 5.0 atomik % La untuk mengesan 500ppm etanol pada suhu 250°C, sedangkan kepekaan SnO₂ tulen hanya adalah 14.84. Peningkatan kepekaan alalah disebabkan oleh pembentukan kristal saiz kecil SnO₂, luas permukaan yang tinggi dan kewujudan keadaan alkali, yang dapat memudahkan proses dehidrogenasi. Peningkatan kandungan La dalam pelet bermangkin sebanyak 7.5 atomik % telah merendahkan kepekaan terhadap etanol. Selain itu, tambahan La dalam sensor SnO₂ menunjukkan selektivitas yang lebih baik untuk etanol daripada metanol dan aseton. Tambahan 5.0 atomik % La dalam SnO₂ telah mempamerkan masa respon sangat pendek 14 saat dengan nilai sensitiviti yang tinggi iaitu 29.9 semasa mengesan 100ppm etanol. Kepekaan pelet sensor adalah bergantung terus kepada kepekatan etanol dalam 100-1500ppm. Sensor

tersebut juga mempamerkan kualiti pengulangan yang tinggi dengan menunjukkan kepekaan yang tinggi selepas digunakan berulang-ulang selama 12 hari. Keputusan kajian ini telah menunjukkan bahawa tambahan La dalam SnO₂ menjadikan ia sebagai sensor VOC yang bagus malah dapat digunakan pada suhu rendah.

PREPARATION, CHARACTERIZATION AND PERFORMANCE OF La DOPED SnO₂ CATALYTIC PELLETS FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS

ABSTRACT

SnO₂ catalytic pellets doped with 0-10 atomic % lanthanum were developed by sol gel method and characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), surface analysis (Nitrogen adsorption-desorption) and scanning electron microscope (SEM). Prior the gas sensor measurement, LabVIEW software was programmed to interface with the electrometer to get all measured electrical resistance values. The electrical resistance change of the catalytic pellets was investigated using volatile organic compound (VOC) vapours i.e. ethanol, acetone and methanol in the air at the temperatures between 150-350°C.

The sensitivity of the SnO₂ catalytic pellet was greatly enhanced by the addition of lanthanum. The sensitivity of 5.0 atomic % La doped in SnO₂ was up to 50.52 for 500ppm ethanol at working temperature of 250°C, while that of pure SnO₂ is 14.84. The improvement in sensitivity may be attributed to the formation of small SnO₂ crystallite size, high surface area and the presence of the basic sites, which facilitated the dehydrogenation process. Increasing of La content in the catalytic pellet up to 7.5 atomic % deteriorated the ethanol sensitivity. Additionally the dopant La in SnO₂ sensors showed good selectivity to ethanol over methanol and acetone. The 5.0 atomic % La-doped SnO₂ exhibited very short response time of 14 seconds with the high sensitivity value of 29.9 for the detection of 100 ppm of ethanol. The linear dependence of the sensitivity on the ethanol concentration is observed in the range of 100-1500 ppm. The gas sensor exhibited high repeatability, reliable

sensitivity after repeated use for 12 days. Our results demonstrated that the dopant La in SnO₂ was promising in fabricated VOC sensors which could work at a low temperature.

CHAPTER 1

INTRODUCTION

Nowadays, air pollution caused by the volatile organic compounds (VOCs) is a major global issue and this problem received much publicity from government and anti-air pollution groups. VOCs are dispersed in the atmosphere and gradually cause harmful effects to human health and plantation as well as the global environment. VOCs are the major contributors to the poor indoor air quality. As most of the people in average spend 80-90% of their time indoor, this can have huge effect upon their health and well-being. This is because inhalation and direct contact of VOCs have been linked to a number of ailments, such as allergies, asthma, cancer, and emphysema (Saravanan, 2004).

Environmental safety regulations on VOCs have been tightened all over the world, as their toxic or carcinogenic natures make them dangerous to human beings. United States Environmental Protection Agency's (EPA's) enlists VOCs as priority pollutants. As the effort to control the VOCs' emission, the Clean Air Act of 1990 calls for a 90% reduction in the emission of 189 toxic chemicals over the next 8 years, and 70% of these being VOCs (EPA, 1990). Therefore, high performance sensors and systems are required to monitor various kinds and quantities of VOCs.

1.1 Volatile Organic Compounds (VOCs)

1.1.1 Definition

Volatile organic compounds (VOCs) are organic chemical compounds that form gases in the atmosphere but under specific conditions they become solid or liquid. Years ago, the U.S EPA assumed that if an organic compound had a vapour

pressure equal to, or greater than 0.1 mm Hg, it should be considered to be a VOC. However, from December 29, 2004, the U.S EPA revising the previous definition and announced the new definition of VOCs as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (EPA, 2004).

The most critical property for the VOCs in the air is they will react with ultraviolet light and nitrogen oxide to form ground level ozone or smog. Ground level ozone is a gas composed of three oxygen atoms at the earth's lower atmosphere. Breathing ozone can cause a variety of health problems including chest pain, coughing, throat irritation and congestion. It may worsen the bronchitis and asthma. Repeated exposure to the ground level ozone may cause permanent lung damage (EPA, 1999a). Therefore, it is very crucial to minimize the release of VOCs into the environment.

1.1.2 Emission Source

The emission sources of the VOCs are mainly divided into two broad categories that are natural activities and anthropogenic. VOCs from the natural give rise to substantial ambient concentrations of organic compound deriving from plants, trees, wild animals, and natural phenomenon such as volcanoes, forest fires decaying the organic matters. The emission of VOC by plants accounts for a significant fraction of carbon fixed by photosynthesis, especially under stress condition. These emissions reduce the amount of carbon that is fixed by vegetation. They take place

on the continental scale and can therefore play a role in atmospheric chemistry even in remote areas (Hewitt et al., 1995).

On the other hand, the anthropogenic VOC emissions come from vehicles, industrial processes, oil refining, land filled wastes, food manufacture and agricultural activities (Derwent, 1995). The common consumer product that cause the VOC emissions are paint, vanish, wax and organic solvents used in cleaning, disinfecting, cosmetic and etc. These products release VOC vapour whenever they are used or stored. Figure 1.1 shows the estimation of the VOCs emissions by source sector in Ontario, Canada in 2007.

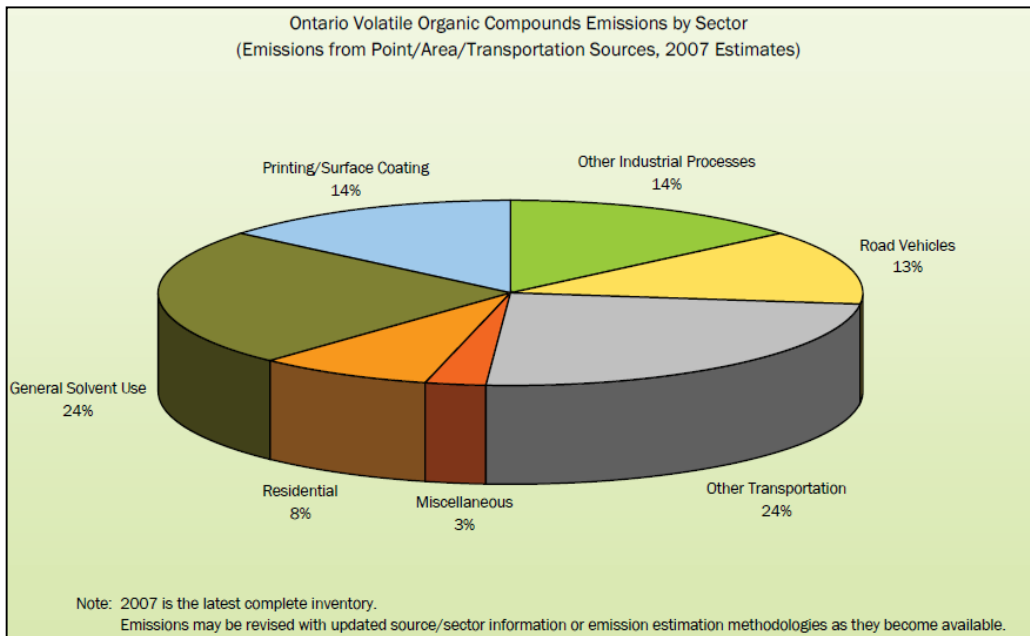


Figure 1.1: Volatile organic compounds emission sector source in Ontario in 2007 (Ontario, 2008)

It is shown that the main emission source of the VOCs is from the on road vehicles and other transportations. It consists of 37% of the total emission of VOCs in Ontario. In this modern society, the motorized transportation such as cars, trucks

and railways are very important for everyone. Movement of people and goods requires energy which mostly relies on the burning of fossil fuels, thus causing the VOCs emissions into the environment and the potentially caused the adverse effects to the people.

Next, solvent used in printing and surface coating industries are contributor to the VOCs emission. Many plant oils can be used as vehicles for pigment in ink, for example toluene, methyl ethyl ketone (MEK), methanol, ethylene glycol and etc. In fact, prior to the early 1960s, soy, corn and canola were common ingredients in ink. However, it had been substituted with petroleum products as the presses could run faster and needed shorter drying times. The solvent used in the printing ink should be reduced in order to protect the VOCs from escaping into the environment.

Besides that, household products also contribute to air pollution through the daily activities and their personal care products. For examples, VOCs that could originate from building materials in our home such as are carpets, adhesives, composite wood products, paints, sealing caulks, varnishes etc. Besides that, there are some examples of VOC in personal care products such as air fresheners, cleaning and disinfecting chemicals, fuels etc. According to the Minnesota Department of Health Fact Sheet that was published in April 2010, generally the level of VOC's indoors is two to five times higher than the level of VOC's outdoors (Minnesota, 2010). Thus, VOCs gas sensor is very important in the human daily life to prevent the inhalation of the VOCs into our body and cause the adverse effects.

1.1.3 Health and Environmental Impact

In atmosphere, VOCs are green house gases (GHG) such as methane and CFC, which cause the global warming. Greenhouse gases in the atmosphere absorb and emit within the thermal infrared range. Greenhouse gases trap heat within the surface-troposphere system to cause global warming (Karl and Trenberth, 2003).

Besides that, the VOCs in the sunlight will react with nitrogen oxides to form ozone and fine particulates. The accumulation of ozone and fine particulates results in smog which will reduce the visibility. The occurrence of smog is more severe under stagnant weather conditions. Smog can irritate eyes, nose and throat and even worsen the respiratory problems such as asthma. Prolonged exposure to severe smog condition may cause permanent damage to lung tissue and affect our immune system (EPA, 1999b). It can also adversely affect plants, animals and materials.

In addition, prolonged exposure of VOCs in the indoor environment may increase the risk of leukaemia and lymphoma (Irigaray et al., 2007). Long-term exposure to VOCs can cause damage to the liver, kidneys and central nervous system. Short-term exposure to VOCs can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment. Many VOCs have distinctive odour, which may become a localized nuisance. The odour of VOCs is likely to be considered an annoyance in the most circumstances even some of them are not harmful.

As a conclusion, the emission of VOCs may cause the adverse effect on human health and environment. In order to ease the problem, the analytical instrument and monitoring system is required to identify and control the emission of VOCs into the atmosphere.

1.2 Analytical Instrumental and Monitoring System

Gas chromatograph (GC) is one of the analytical instruments and monitoring unit that is widely used to identify the VOCs components. GC is common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. A gas chromatograph uses a flow-through method where the different chemical constituents of a gas sample pass through the narrow tube (column) at different rates depending on their various chemicals and physical properties and their interaction with the column filling. The chemicals will exit at the end of column and the components in the gas sample is detected and identified electronically. The GC is specific with high sensitivity toward the organic pollutants (Dewulf et al., 2002).

Other than that, mass spectroscopy (MS) and Fourier Transform Infrared (FTIR) instruments can also be used to detect the presence of hazardous gas. MS identify gas molecules through characteristic variable deflections from a magnetic field. FTIR uses infrared spectral characteristics of gases to differentiate the gas molecules in the environment. These analytical instruments are sensitive to identify the gas molecules. However, they are only applicable in a laboratory environment. They require skilled and trained operators and generally are very expensive. These instruments are also large in size and often need high maintenances to maintain their

sensitivity toward the gas components. Therefore, these analytical instruments are not suitable for monitoring of air quality and safety in the environment and a portable gas sensor is more suitable for this purposes. The following section discusses about the gas sensor technology and the available types of gas sensor.

1.3 Gas Sensor Technology

A gas sensor is a transducer that detects gas molecules and produces an electrical signal with a magnitude proportional to the concentration of the gas (Kumar et al., 2010). There are five types of gas sensors that are electrochemical, catalytic combustible, infrared, photoionization and solid state gas sensors. These gas sensors are suitable and widely used as gas monitors for maintaining area air quality and safety. All of these gas sensors are suitable to be used for the detection of toxic and combustible gases in the work area. The uses of gas sensors are crucial for human and property protection and also process control.

1.3.1 Electrochemical Sensors

Electrochemical sensors operate by reacting with the gas of interest to produce an electrical signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensor electrode and a counter electrode separated by a thin layer of electrolyte. The electrochemical also consists of a hydrophobic membrane to prevent the electrolyte from leaking out of the sensor and also filter out the water content in the sample gas. The gas diffuses through the hydrophobic membrane to react on the surface of the sensing electrode through either an oxidation or reduction mechanism. These reactions are catalyzed by electrode materials specially developed for the gas of interest. With a resistor connected across

the electrodes, a current proportional to the gas concentration flows between anode and the cathode. The current can be measured to determine the gas concentration. Electrochemical gas sensor is also described as an amperometric gas sensor or a micro fuel cell(Chou, 2000). The typical electrical gas sensor setup is shown in Figure 1.2.

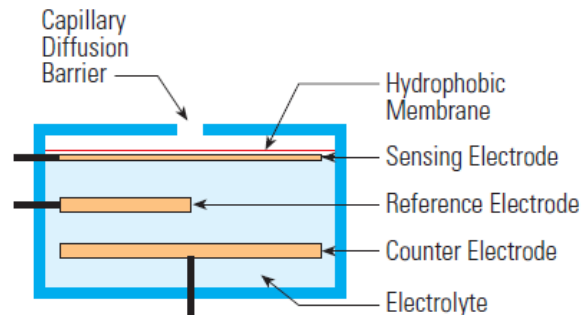


Figure 1.2: A typical electrochemical sensor setup (Chou, 2000)

Electrochemical gas sensors are generally fairly selective to the target gas they are designed for. The degree of selectivity depends on the type of sensor, the target gas, and the concentration of gas the sensor is designed to detect. The best electrochemical sensor is for the detection of O_2 , which has good selectivity, is very reliable, and has a long life expectancy.

1.3.2 Catalytic Combustible Gas Sensors

Catalytic combustible gas sensors are used to detect combustible gases. Catalytic combustible sensor consists of a single platinum wire covered with catalytically-treated metal oxide. The combustible gas mixture will start to burn or ignite at lower temperature than their normal ignition temperature in the presence of the catalytically metal oxide. Therefore, this gas sensor is also known as catalytic combustion. The gas sensor will give the signal by the electrical conductivity of the

material as the temperature of the material changed (Chou, 2000). A typical catalytic bead sensor setup is shown in Figure 1.3.

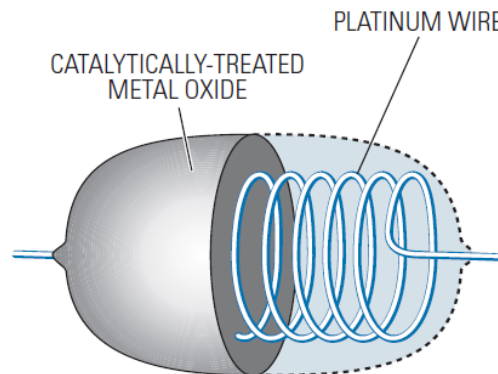


Figure 1.3: A typical catalytic bead sensor setup (Chou, 2000)

Catalytic combustion gas sensor may deteriorate when it is exposed to excessive concentration of gases and extreme temperature. This gas sensor may also lose its sensitivity whenever it is exposed to certain chemicals such as sulphur, chlorine and heavy metal that may deactivate the catalytic sensor. Furthermore, the quality of the catalytic sensor is relatively important to make sure the effectiveness in its application as a gas sensor.

1.3.3 Infrared (IR) Gas Sensors

An infrared (IR) gas analyzer measures trace gases by determining the absorption of an emitted infrared light source through a certain air sample. Gas molecules can be identified using their absorption characteristics. A library of the spectroscopy scan can be stored inside the instrument. When a sample gas is scanned by the infrared gas analyzer, the graph is compared with the stored curves to identify the gas molecules. IR analyzer is often used to detect the combustible, corrosive and reactive gases (Rogalski, 2002).

The main advantage of an IR analyzer is that the detector does not directly interact with the gas to be detected. The IR analyzer can have a life expectancy for more than 10 years. However, the IR analyzer cannot monitor all gases and only able to monitor the nonlinear molecules such as methane. Moreover, it can be easily affected by humidity and water. The dust and dirt can coat the optics and impair the response of the IR sensor. The size of IR sensors is commonly on a laboratory scale to provide a good resolution to the signal.

1.3.4 Photoionization Gas Sensors

The photoionization detector (PID) utilizes ultraviolet light to ionize gas molecules. In the ambient, nitrogen, oxygen, carbon dioxide and water vapour have high ionization energies of 15.6, 12.1, 13.8 and 12.6 eV, respectively while the noxious substances such as benzene, toluene and phenol have low ionization energies of 9.2, 8.8 and 8.5 eV, respectively. These noxious substances will get ionized by UV light at 11.8 eV. The ionized molecules are detected by applying a high voltage between an anode and a cathode. The current generated is measured and indicates the concentration of the contaminant substance (Liess and Leonhardt, 2003).

PID instruments offer very fast response, high accuracy and good sensitivity for detection of low ppm volatile organic compounds (VOCs). However, the PID lamp requires frequent cleaning. The lamp window is directly exposed to the sample gas; therefore the condition of the window is very critical to provide the accurate reading. The life expectancy of the PID instruments is depends on the types of lamp that been used. The presence of humidity in the examined air can cause the window to degrade and can reduce the sensitivity of the PID instruments. (Chou, 2000)

1.3.5 Solid- State Gas Sensors

A solid-state gas sensor consists of one or more metal oxides from transition metals, such as tin oxide, zinc oxide and etc. These metal oxides are prepared and processed into pastes which are used to form thick or thin chip sensors. Solid state gas sensor is also known as Semiconductor Gas Sensor (SGS) or Metal Oxide Sensor (MOS). Usually, a heating element is needed to regulate the sensor temperature as sensors exhibit different gas responses. In the presence of hazardous gas, the metal oxides cause the gas to dissociate into charged ions or complexes which result in the transfer of electrons. The gas sensor can give the signal by the changes of the conductivity resulting from the interaction of the gas molecules with the metal oxide surface. A heating element is needed to heat the metal oxide material to an operational temperature range that is optimal for the gas to be detected (Chou, 2000).

Solid-state sensors are the most versatile sensors, as they can detect a wide variety of gases. A solid stated sensor has a very long life expectancy and long lasting in clean applications.

1.4 Application of Gas Sensor

Gas sensors have found widespread applications in the domestic and industry. Table 1.1 shows the applications of gas sensors in various fields. The gas sensors are important for fire detectors, leakage detectors, and controllers of ventilation in cars and planes and alarm devices. Other than that, gas sensors are used to detect the VOCs or smells or smoke from the food and household products. Gas sensors are crucial to maintain the indoor air quality.

Table 1.1: Examples of applications for gas sensors (Capone et al., 2003)

Applications	Purposes/Function
Automobiles	<ul style="list-style-type: none"> • Car ventilation control • Filter control • Gasoline vapour detection
Safety	<ul style="list-style-type: none"> • Alcohol breath tests • Fire detection • Leak detection • Toxic/ flammable/ explosive gas detectors • Boiler control • Personal gas monitor
Indoor air quality	<ul style="list-style-type: none"> • Air purifiers • Ventilation control • Cooking control
Environmental control	<ul style="list-style-type: none"> • Weather stations • Pollution monitoring
Food	<ul style="list-style-type: none"> • Food quality control • Process control • Packaging quality control (off-odours)
Industrial production	<ul style="list-style-type: none"> • Fermentation control • Process control
Medicine	<ul style="list-style-type: none"> • Breath analysis • Disease detection

1.5 Problems Statement

Despite efforts to reduce the emission of volatile organic compounds (VOCs) from many sources, exposure to these hazardous substances remains to be a public health issues. Over exposure to VOCs can cause eye, nose and throat irritation; headaches, nausea and skin allergy reaction. Meanwhile, inhaling VOCs such as benzene, toluene and xylene are dangerous and likely to cause cancer. Development of simple but novel and low cost VOCs detection devices are not popular until recently, when the devices have been studied intensively for domestic and industrial usage. The sensitivity, selectivity and stability are the most important parameters in the study for further development and improvement of the sensing devices.

Semiconductor based materials have shown a great potential for wide range of applications. Metal oxides such as SnO₂, ZnO, WO₃ and TiO₂ have been reportedly applicable as gas sensors in previous studies (Zhu et al., 2004; Zhao et al., 2006; Alessandri et al., 2007; Khadayate et al., 2007). Among these metal oxides, tin dioxide SnO₂ has been proven to be one of the most attractive metal oxides for gas sensor application owing to its chemical stability and gas sensitivity. It is known that by modifying the metal element or by doping of noble metals such as Pt, Pd or rare earth metal, the sensitivity and selectivity toward certain gases can be enhanced (Esfandyarpour et al., 2004; Choi et al., 2008). These dopants act as catalysts and surface sites for adsorption of oxygen. The dopants bring about improvement in porosity, thermal stability and gas sensing characteristics in gas sensing matrix (Korotcenkov et al., 2004).

In the present work, rare earth element, i.e. lanthanum, was used as a catalyst to enhance the sensitivity of the SnO₂. Various methods of La-doped SnO₂ sensors have been reported (Jinkawa et al., 2000; Stambolova et al., 2000; Van Hieu et al., 2008). However, the most common is by use of tin (IV) isopropoxide and La(CH₃CHOO)₃ as precursors in the sol gel and impregnation methods (Kugishima et al., 2006; Mihaiu et al., 2007) to produce La-doped SnO₂ sensor. Therefore, a new combination of tin tetrachloride and lanthanum nitrate has been used as the precursors in sol-gel method. The sensitivity experiment of La-doped SnO₂ towards ethanol, methanol and acetone was carried out and compared against pure SnO₂ to study the effect of La on the sensitivity. The sensitivity of the sensors was studied at different atomic ratios of the metal loading, calcination temperatures, different types

of VOCs and ethanol vapour concentrations. The response and recovery time were also measured to study the viability of La-doped as a sensor.

1.6 Objectives

The present study has the following objectives:

- a) To develop suitable catalytic pellets based on metal oxide that can be used to detect VOCs.
- b) To characterize the catalytic pellets using standard methods for the purpose of comparisons and understand of their properties.
- c) To perform VOCs detection in order to measure the conductivity, sensitivity, response time, recovery time of the developed catalytic pellets.

1.7 Scope of Study

In the present study, tin dioxide (SnO_2) was identified to be used as the metal oxide for the catalytic pellets. The selection of the SnO_2 was based on its high sensitivity, high chemical stability under harsh conditions, low cost in fabrication and successful application as sensing material by other researchers. The synthesis of SnO_2 powders was carried out using tin chloride pentahydrate via sol-gel method. The sol-gel method was chosen due to it can improve the homogeneity, stability, surface area and porosity of the sensing materials.

The gas sensing properties of the SnO_2 based sensor can be enhanced by adding dopant into the sensing materials. In this study, the dopant that had been chosen was lanthanum (La). Lanthanum was successfully incorporated into the SnO_2 powder with the in-situ method. The parameters investigated in this study were the

effect of the metal additive loadings (0- 10 atomic %) and calcination temperatures (500-900°C). Optimization was done to obtain the best catalytic pellet that can be used as the VOCs gas sensor with the high sensitivity, high stability and fast response time. The studied parameters were the influence of porosity, surface area and crystallinity on the sensitivity of the sensor catalytic pellet. The prepared metal oxide gas sensors were characterized with X-ray diffraction (XRD), transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET) surface area analysis and scanning electron microscope (SEM). With the characterization, the physiochemical of the catalytic pellet could be further correlated with the sensitivity of the gas sensor.

The gas sensing behaviours were observed in the gas sensor measurement unit that had been upgraded with a data logging system. The gas sensor measurement unit consisted of two major parts that were bubbler VOCs liquid and gas chamber connected to the electrometer. In this study, hazardous VOC vapours such as ethanol, methanol and acetone were used as the model organic pollutants to be detected. The concentration of VOC vapours was analyzed using a gas chromatograph before the VOC vapours was injecting into the gas chamber for the gas sensor measurement. The parameters studied in the measurement unit were operating temperatures (150-350°C), different type of VOC vapours (ethanol, methanol and acetone) and with different ethanol concentrations (100- 1500 ppm), response and recovery times and last but not least the stability or reliability of the catalytic pellets. The performance of the gas sensor was based on their conductivity or electrical resistance in the different conditions.

1.8 Organization of the Thesis

Generally, the thesis consists of five chapters. Chapter 1 gives an outline of the whole thesis which covers the introduction to air pollution, definition of VOCs, VOCs emission sources and their impacts toward human being and environment. Then, the analytical and air monitoring systems, gas chromatography are usually used to identify the presence of VOC are discussed by highlighting their pros and cons. Next, the current gas sensor technology to control and monitor the VOCs in domestic and industrial is described in detail. The chapter also encloses with problem statements that illustrate the problems faced and the necessity to carry out the current research study. The scopes of study elaborate the objectives in details and provide the focus and boundaries of the study. Organization of the thesis winds up the first chapter.

Subsequently, Chapter 2 compiled all literature reviews conducted on semiconductor gas sensor researches. Brief explanations of semiconductor metal oxide based gas sensor and types of metal oxide gas sensor are described. The methods for SnO₂ gas sensor preparation are discussed. The sensing characteristics of SnO₂ and the role of additives toward the SnO₂ are also covered.

Chapter 3 presents the experimental methodology and analysis. The details of chemicals and materials used throughout the study are given. Besides, this chapter also provides the details on sensor measurement rig set-up, catalytic pellet preparation, catalytic pellet characterization, sensor performance measurement and optimization of the sensor performance.

Chapter 4 comprises of results and discussion of the study. Effects of the parameters on the preparation of sensing material and detection activity are discussed. Besides that, characteristics of the gas sensor material such as crystallinity, morphology, surface area, grain size are further discussed and correlated with the gas sensor performance.

Chapter 5 provides a summary of the results obtained in the present study. Besides, concluding remarks and recommendations for the future works in gas sensor technology are also discussed.

CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

Gas sensor plays important roles in monitoring and controlling the safety of chemical processes in the domestic and industrial environments. Since the first metal oxide sensor developed by the Taguchi in year 1971, a lot of efforts have been invested to further optimize the sensors performance, to lower the cost of fabrication and to simplify the prototype to be used in the real-world environment. The working principle of a typical resistive metal oxide gas sensor is based on a shift of the equilibrium of the surface oxygen reaction due to the presence of the target gas. The resulting change in the concentration of chemisorbed oxygen is recorded as a change in resistance of the gas sensing material that is defined as the sensitivity of the gas sensor (Korotcenkov, 2008). The detection of the toxic and flammable gases is a subject that is gaining importance in domestic and industry to keep our environment clean and lively.

The present study is focused on the development of metal oxide gas sensor (MOS) based on the tin dioxide (SnO_2). In this chapter, the metal oxide gas sensors are discussed thoroughly with a particular focus on their characteristics and their sensing mechanisms. It is followed by the types of metal oxide gas sensor that is commonly used by other researchers. Table 2.1 shows the summary of metal oxide sensors used for VOCs detection. Other than that, the structural and the gas sensor properties on the metal oxide gas sensing based on SnO_2 are described. Next, the role of the additives on metal oxide that can be used to detect the VOCs is reported.

Table 2.1: Summary of metal oxide sensors used for VOCs detection

Metal oxides	Method of preparations	Target gas	Operating Temperature for Maximum sensitivity (°C)	References
SnO ₂ (Nanorods & hollow speheres)	Solvothermal reaction	Ethanol 10-1000 ppm H ₂ S 5-100 ppm	25	Xu et al. (2009)
SnO ₂ (Nanowires)	Polyol mediated reaction	CO 100 ppm C ₃ H ₈ 200 ppm Ethanol 200 ppm Acetone 200 ppm	400	Park and Lee (2009)
La ₂ O ₃ -SnO ₂	Hydrothermal synthesis	Ethanol 10-1000 ppm	200	Shi et al. (2009)
Au-SnO ₂	Successive Ionic Layer Deposition (SILD)	CO 2000 ppm H ₂ 2000 ppm	450	Korotcenkov et al. (2009a)
Fe-SnO ₂	Electrospinning method	Ethanol 100 ppm	300	Wang and Liu (2009)
WO ₃	Screen Printing	Ethanol 25-100 ppm	400	Khadayate et al (2007)
WO ₃	Commercial Powder	Ethanol 100 ppm	160	Yu-De et al. (2001)
Cr-WO ₃	Sol-gel	NH ₃ 100-1000 ppm	350	Ruiz et al. (2006)

Table 2.1: Continued

Metal oxides	Method of preparations	Target gas	Operating Temperature for Maximum sensitivity (°C)	References
Anatase TiO ₂	Flame spray pyrolysis	Ethanol 1-75 ppm Isoprene 1-75 ppm Acetone 1-75 ppm	500	Teleki et al. (2006)
TiO ₂	Chemical precipitation	Ethanol 20-200 ppm Acetone 20-200 ppm	350	Rella et al. (2007)
TiO ₂ -SnO ₂	RF sputtering	H ₂ 100-20000 ppm	300	Zakrzewska and Radecka (2007)
ZnO	Chemical Precipitation	Ethanol 100 ppm Acetaldehyde 100 ppm H ₂ 500 ppm CO 500 ppm <i>i</i> -C ₄ H ₁₀ 500 ppm Ethylene 500 ppm	332	Xu et al. (2008)
Tetrapod-shaped ZnO	Vapor phase oxidation	Benzene 100 ppm Toluene 100 ppm Acetone 100 ppm Alcohol 100 ppm	320	Zhu et al. (2005)

2.2 Semiconductor Metal Oxide Gas Sensor

Numerous researchers have shown their interest in the development of the semiconductor metal oxide gas sensors. These semiconductor gas sensors have the desirable features such as simplicity in device structure, reduced size, low cost and robustness in practical applications. In order to ensure the practicality of the sensor in domestic and industrial applications, there are many designs on thick and thin film sensors that have been investigated. Some of the sensors are micro-fabricated to minimize their size. Figure 2.1 shows the examples sensor devices that been investigated by previous researches.

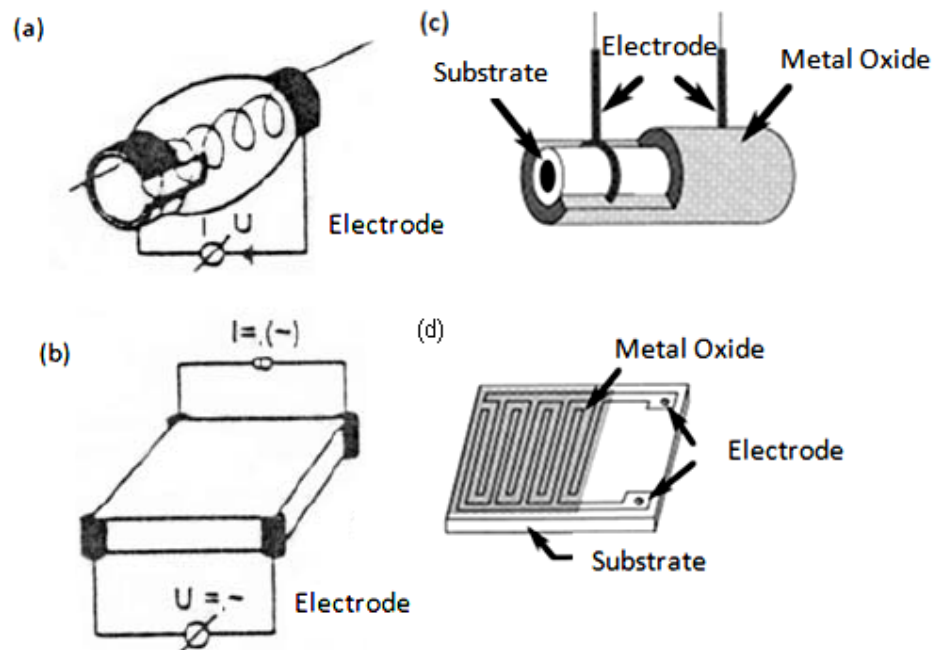


Figure 2.1: Schematic drawing of sensor devices: (a) a sintered ceramic sensor with embedded wires; (b) a sensor with a four-point probe arrangement; (c) block types; (d) thick or thin film type (Yamazoe et al., 2003; Trimboli, 2005)

Figure 2.1 (a) depicts a sintered ceramic with heater wires embedded inside the material and two external contacts. It is the earliest device made for electrical sensor. Figures 2.1(b) illustrates one type of four-point arrangement which two of the contacts in this measurement are used for current flow, while the other two are used

to make a potential measurement in the absence of current. Figure 2.1(c) and (d) shows metal oxide sensor in block or film type device with electrodes either embedded or interdigitated under the metal oxide. However, the devices for the laboratory tests are usually furnished with an external heater so that they are heated externally to obtain an optimum operating temperature.

Electro-physical properties of the materials are the key factors that make the metal oxide suitable to be used as a gas sensor. Big band gap (E_g) and small activation energy of the centers is an optimal combination of parameters for the materials designed for semiconductor solid-state gas sensors. Such correlation of activation energies is necessary to avoid the sensor's operation in the region of self conductance. As reported by Korotcenkov (2007), the optimal band gap for the metal oxide must be higher than $2.5eV$ to operate at a temperature exceeding 300°C . Table 2.2 shows the band gaps of various sensing materials. Hence, it can be concluded that those well-known metal oxides satisfy the requirement for a gas sensor criterion.

It is necessary to note that an opportunity to operate at higher temperature is an important advantage of solid-state semiconductor gas sensors, because this fact considerably reduces the influence of air humidity on gas-sensing characteristics. It was established that, the lower the operating temperature, the greater the sensitivity of the sensor's parameters to relative air humidity (Korotcenkov, 2005). The big band gap is also a sufficient advantage for metal oxides with ionic conductivity. It is because the contribution of electron conductivity in sensing materials is reduced, especially at high operating temperatures. The band gap for n-type oxides may act as donor band while p-type oxides act as acceptor bands as shown in Figure 2.2.

Table 2.2: Band gap of metal oxide sensing materials (Korotcenkov, 2007)

Metal oxides semiconductor	Band gap (eV)
MgO, CaO, Al ₂ O ₃ , SiO ₂ , TeO ₂	> 6.0
SrO, Y ₂ O ₃ , HfO ₂ , ZrO ₂	5 – 6
BaO, La ₂ O ₃ , CeO ₂ , Ga ₂ O ₃	4 – 5
TiO ₂ , Nb ₂ O ₅ , Ta ₂ O ₅ , ZnO, In ₂ O ₃ , SnO ₂	3 – 4
V ₂ O ₅ , Cr ₂ O ₃ , WO ₃ , NiO, Fe ₂ O ₃	2 – 3
Co ₃ O ₄ , PdO, CuO, Sb ₂ O ₃	1 – 2

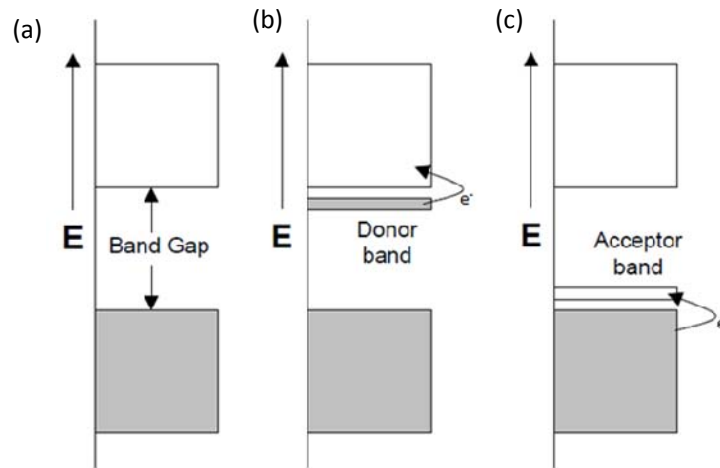


Figure 2.2: Band gap structure of (a) an insulator, (b) an n-type semiconductor (c) a p-type semiconductor (Trimboli, 2005)

It is known that gas sensing materials can have either n-type or p-type of conductivity. The classification of metal oxides based on the type of conductivity is summarized in Table 2.3. Semiconductor of n-type and p type have inversed direction of conductivity's change upon interaction with the same gases. For n-type materials, the conductivity drops with a growth in oxygen pressure, whereas for p-type oxides, it increases.

Table 2.3: Classification of metal oxides based on type of conductivity (Korotcenkov, 2007)

Type of conductivity	Metal oxides
n-type	MgO, CaO, TiO ₂ , ZrO ₂ , V ₂ O ₅ , Nb ₂ O ₅ , Ta ₂ O ₅ , MoO ₃ , WO ₃ , ZnO, Al ₂ O ₃ , Ga ₂ O ₃ , In ₂ O ₃ , SnO ₂
p-type	Y ₂ O ₃ , La ₂ O ₃ , CeO ₂ , Mn ₂ O ₃ , Co ₃ O ₄ , NiO, PdO, Ag ₂ O, Bi ₂ O ₃ , Sb ₂ O ₃ , TeO ₂
n, p-type	HfO ₂ , Cr ₂ O ₃ , Fe ₂ O ₃ , CuO

It is noted that those tin oxide (SnO₂), zinc oxide (ZnO), tungsten oxide (WO₃) and titanium oxide (TiO₂) that are commonly used for the fabrication of gas sensor materials are classified into the n-type semiconductor conductivity. Generally, n-oxides are thermally stable and have the possibility to work at lower oxygen partial pressure as compared to p-type oxides. It is known that p-type oxides are relatively unstable because of the tendency to exchange lattice oxygen easily with air. However, it does not mean that the p-type oxides are not applicable for sensor design. There is a research based on the Cr_{2-x}Ti_xO₃ (x<0.4) (CTO) as H₂S and CH₄ gas sensor design (Pratt and Williams, 1997). Fe₂O₃ also been used as effective additive to indium oxides to form nano-composite based sensors with extremely high conductivity response to H₂S (Ivanovskaya et al., 2003).

Besides, the direction for sensor's resistance change for n-types oxides during detection of reducing gases is preferred due to the simpler compatibility with peripheral measuring devices and better reproducibility of output signal (Korotcenkov, 2007). The n-type oxides sensor resistance decreases when interaction with reducing gases occurs while it is vice versa for p-type oxides. Whereas for the oxidation gases, the sensor's resistance increase for the n-types oxides and decreases for the p-type oxides. Therefore, in this study, SnO₂ had been chosen as the metal

oxide to be used as gas sensing material. SnO₂ is categorized into the n-type semiconductor with the preferred output signal in detecting reducing gases.

2.3 Gas Sensing Mechanism

After understanding the semiconductor metal oxide gas sensor structure, the gas sensing mechanism is necessary to be noted as the gas sensing mechanism involved is fairly complex. The gas sensing mechanism starts with the surface interaction between gas and metal oxide is based on the grain boundaries of the polycrystalline oxide film. Generally, the gas sensing mechanism of semiconductor metal oxide are dominated by either bulk processes or surface processes. For the bulk processes, the operating temperatures of the sensors are high i.e. exceeding 600°C, while for the surface processes, the operating temperatures are below 400°C (Rothschild et al., 2000).

Detail bulk and surface processes, generally include reduction/oxidation processes of the metal oxide, adsorption of the chemical species directly on the metal oxide and/or adsorption by reaction with surface states associated with preadsorbed ambient oxygen. Then, electronic transfer of delocalized conduction-band electrons to localized surface states occurs and vice versa. Next, catalytic effects and in general complex surface chemical reactions between the different adsorbed chemical species should be considered. Schematic representation of these processes for physiochemical properties of metal oxides are shown in Figure 2.3 (Korotcenkov, 2007).